Material Technologies Developments for Solar Hydrogen

C. Agrafiotis, C. Pagkoura, S. Lorentzou, J.C. Hoguet and A. G. Konstandopoulos
Aerosol and Particle Technology Laboratory, Chemical Process Engineering Research Institute, Center for Research and Technology-Hellas (CERTH/CPERI), P.O. Box 361, 57001 Thermi-Thessaloniki, Greece; E-mail: chrisagr@cperi.certh.gr

ABSTRACT:
The present work presents recent activities of our Laboratory in the field of solar-aided hydrogen production materials and reactor technologies that can be fully integrated into solar thermal power plants. Emphasis is given on structured monolithic solar reactors where ceramic supports optimized to absorb solar radiation and develop sufficiently high temperatures, are coated with active materials to perform a variety of “solar-aided” reactions such as water splitting or natural gas reforming. Particular examples discussed include properties’ assessment of monolithic ceramic honeycombs used as volumetric solar thermal reactors/receivers, synthesis of active water-splitting redox materials for the production of hydrogen and their tailored deposition upon porous supports and design, operation simulation and performance optimization of structured monolithic solar hydrogen production reactors.

KEYWORDS: solar hydrogen, water-splitting, redox materials, honeycomb reactors, solar chemistry

Introduction
Concentrated Solar Thermal Power (CSP) plants are a highly viable alternative to fulfill the world’s future needs for clean electrical energy, significantly increasing in parallel the share of renewable energy in the total primary energy supply. The electricity produced by such thermal concentrating systems combined with the innovative technology of solar volumetric receiver systems is one of the most promising techniques for the future. The harnessing of the huge energy potential of solar radiation and its effective conversion to chemical energy carriers such as hydrogen is a subject of primary technological interest. Hydrogen can be solar-aided produced via from a variety of fossil and non-fossil fuels via different routes such as water splitting (to produce hydrogen and oxygen) [1-5], natural gas steam reforming (to produce syngas) [6-11] and natural gas cracking (to produce hydrogen and carbon black nanoparticles) [12-14]. Current engineering challenges in the field of “solar chemistry” include the development of advanced solar concentrators and high-temperature, high-flux measurement techniques, synthesis of active materials for solar chemistry reactions (catalysts, redox materials) and design and operation of novel receiver/reactor systems capable to collect effectively the concentrated solar radiation and at the same time to perform in an efficient and elegant manner the high-temperature reactions mentioned above.

Despite basic research with respect to active redox and catalytic materials, solar reactor concepts have only recently been reported in the literature [15]. Some are based on particles fed into rotating cavity reactors, concepts that are complicated and costly to operate. On the other hand, porous solids like extruded monoliths with parallel channels and thin walls made from various ceramics, ceramic foams and metal structures have been widely used in the automotive exhaust after-treatment applications for the performance of high-temperature reactions employing both gaseous and particulate reactants (CO/CO₂, HCs, NOx and soot particulates). The advantages offered by such structures such as thin walls, high geometric surface area and therefore good gas-solid contact, low pressure drop, good mass transfer performance and ease of product separation [16] can be combined with special material properties such as thermal shock resistance and mechanical strength to couple the collection and exploitation of solar energy with efficient reactor concepts. Such porous solids can operate as open volumetric receivers of concentrated solar radiation to heat the reactant gases as they flow through their porous structure. For example the absorbance of Silicon Carbide (SiC) coupled with its high thermal conductivity enables the collection of solar heat and effective heating of the reactant gases inside the honeycomb channels - it has already been demonstrated that SiC monoliths can act as collectors of solar heat and achieve temperatures in excess of 1100 °C [17,18]. Provided that catalytic and redox materials effective and durable at these temperature levels can be synthesized, a variety of solar chemistry reactions can be performed with such materials immobilized upon the porous support walls avoiding the needs of continuous powder feeding and collection from the reactor.
During the last six years, our Laboratory has developed a significant activity in the field of solar chemistry, by developing advanced materials and technologies for solar hydrogen production systems with emphasis on structured monolithic solar reactors where ceramic supports optimized to absorb solar radiation and develop sufficiently high temperatures, are coated with active materials to perform a variety of “solar-aided” reactions such as those mentioned above. Particular successful examples of such materials and technologies developed that can be fully integrated in solar thermal power plants include:

- Pilot-scale synthesis of active water-splitting redox materials that can achieve splitting of water and production of hydrogen at relatively low temperatures and are capable for regeneration and re-use.
- Tailored deposition of powders on porous supports.
- Assessment of monolithic ceramic honeycombs used as volumetric solar thermal reactors/receivers.
- Design, simulation and performance optimization of structured monolithic solar hydrogen production reactors including mathematical modelling of transport processes and chemical reactions, operation simulation and design optimization.

Some aspects of these developments are presented below.

**Synthesis of active materials**

One of the reactions with tremendous economical impact because of the low value of its reactants is the dissociation of water (water splitting) to oxygen and hydrogen. The combination of active materials that can split water at relatively low temperatures with concentrated solar irradiation systems is considered of immense value and impact on the energetics and economics worldwide and by some as the most important long-term goal for the production of “solar fuels” to cut hydrogen costs and ensure virtually zero CO₂ emissions [19]. The current state of the art of solar chemistry for water splitting and hydrogen production is the thermochemical two-step water splitting process using redox systems. According to this scheme, during the first step (water splitting) the reduced and therefore activated material (usually a metal oxide) is oxidized by taking oxygen from water and producing hydrogen. During the second step (re-generation) the material is reduced to be used again, delivering some of its lattice oxygen and hence a cyclic operation is established:

\[
\text{MO}_{\text{reduced}} + \text{H}_2\text{O} (g) \rightarrow \text{MO}_{\text{oxidized}} + \text{H}_2(g) \quad \text{...(1)} \quad \text{MO}_{\text{oxidized}} \rightarrow \text{MO}_{\text{reduced}} + \frac{1}{2} \text{O}_2 \quad \text{...(2)}
\]

The redox materials that have been evaluated consist of oxide pairs of multivalent metals (Fe₃O₄/FeO, Mn₃O₄/MnO) or systems of metal oxide/metal (e.g. ZnO/Zn) [20], the most representative of which can be considered the Fe₃O₄/FeO system [21]. Water splitting is taking place at temperatures below 900K while the reduction of the metal oxide, i.e. the regeneration, takes place at much higher temperatures. The concept has been proven experimentally, however the regeneration temperatures are still high imposing a barrier towards integration of a two-step water splitting process with a concentrating solar system. For full exploitation of the potential of such cycles, there is a need for materials with high water-splitting activity and regenerability at moderate temperatures, with long-term stability and no properties’ degradation over extended cyclic operation under concentrated solar irradiation.

With this perspective, redox water-splitting materials based on doped-iron oxides were synthesized in our laboratory via three “non-traditional” routes: Self-Propagating High-Temperature Synthesis (SHS), Gel Combustion (GC) and Aerosol Spray Pyrolysis (ASP). These synthesis methods were chosen with the rationale that they share the common characteristics of very short synthesis times and extremely high cooling rates and therefore are capable of producing particles with high defects concentration; in addition they can also take place within reactors that allow for controlled oxygen partial pressure, therefore “tuning” further the product oxygen vacancies concentration. Additional common advantages are potential for nanoparticle synthesis, ease for precisely controlled doping, no requirement of sintering at high temperatures and amenability to scale-up. The synthesis details have been reported previously [22, 23], therefore only the general reaction concepts are reported below, where A and B denote the bivalent dopant metals either Ni, Mn or Zn. For comparison purposes, materials of similar compositions were also synthesized via the «traditional» solid-state synthesis (SSS) route by co-firing of the component oxides under air at 1200 °C for 8 hrs and comparatively evaluated.

i) SHS (or Combustion Synthesis) of the targeted materials is based on the heat released from the reaction of iron metal powder (“fuel”) with oxygen (“oxidizer”) in the presence of the dopant metal oxides and of Fe₂O₃ powder as a “thermal ballast/moderator” to control the synthesis temperature, according to the scheme:

\[
2k \text{Fe} + (1-k) \text{Fe}_2\text{O}_3 + x \text{AO} + y \text{BO} + (1.5 \text{ k}) \text{O}_2 \rightarrow (\text{A}_x\text{B}_y)\text{Fe}_2\text{O}_4 \quad \text{...(3)}
\]

The synthesis times were of the order of few seconds, whereas by adapting the reaction conditions, the product phase composition varied between that of spinel (AₓBₙ)Fe₂O₄ and doped wustite (AₓBₙFe₁₋ₓ₋ₙO). ii) Gel combustion is based on the reaction in aqueous solutions of nitrate salts Aₓ(NO₃)ₙ, (“oxidant”) with amino-groups (“fuel”) to form ammonium nitrate that is explosive upon heating. Soluble organic substances like citric acid or glycine are added to form stable chelates with the metal ions in solution preventing selective...
synthesis temperature and the residence time in the synthesis reactor. Their size depends on the solution properties, the nebulizing process, the dimensions of the order of few tens of nanometers (50-100 nm). Products from SHS form dense, sintered grains (Fig. 1d). Larger magnifications (Fig. 1c) demonstrate that these agglomerates consist of much smaller grains with dimensions of the order of few tens of nanometers (50-100 nm). Products from SHS form dense, sintered grains (Fig. 1d). ASP produced powders are inherently spherical (Fig. 1e) and very fine (of the order of few hundreds of nanometers); their size depends on the solution properties, the nebulizing process, the synthesis temperature and the residence time in the synthesis reactor.

iii) Aerosol spray pyrolysis (ASP) employs the atomisation of a solution of the metal precursor salts in a spray of fine droplets that is subsequently passed through a hot-wall reactor where it transforms within a very short time to ultra-fine, spherical particles [24]. The ASP experiments took place with aqueous solutions of Fe, Zn, Mn and Ni nitrates with the addition of organic chelating agents, in a stainless steel reactor, heated between 350-1070 °C. The carrier gas was air and the residence time about 1 sec. Under these synthesis conditions, the reaction scheme is the same as that of Eq. (4) and the synthesized products were always of the spinel crystal structure \((A_B)_x\)Fe\(_2\)O\(_4\).

A comparison of the XRD spectra of materials synthesized via the various routes is shown in Fig. 1a. Depending on the synthesis route, the product can be from single-phase spinel either very well or much less crystallized (SSS, ASP respectively) or a mixture of wustite and spinel (SHS under vacuum). Typical SEM pictures of products from the various routes are shown in Figs. 1b-d. “As-synthesized” powders from GC form large agglomerates of the order of 50 μm, full of large pores due to the violent expulsion of gases (Fig. 1b). Larger magnifications (Fig. 1c) demonstrate that these agglomerates consist of much smaller grains with dimensions of the order of few tens of nanometers (50-100 nm). Products from SHS form dense, sintered grains (Fig. 1d). ASP produced powders are inherently spherical (Fig. 1e) and very fine (of the order of few hundreds of nanometers); their size depends on the solution properties, the nebulizing process, the synthesis temperature and the residence time in the synthesis reactor.

Figure 1: Phase composition and morphology comparison among products synthesized from the various routes: (a) XRD comparison, (b)-(e) SEM pictures: (b) GC (c) GC (higher magnification), (d) SHS, (e) ASP.

All these materials were evaluated with respect to their capability for water-splitting and total hydrogen yield in a special laboratory unit described previously [25]. Systems from all the synthesis routes were able to split water and generate hydrogen as the only product, at temperatures as low as 800°C and could be repeatedly regenerated under inert atmospheres at temperatures below 1200°C [23]. The “best” products from each synthesis route are compared with respect to water-to-hydrogen conversion and total hydrogen yield in Figs 2a, 2b respectively. Both SHS and ASP materials exhibited very high water conversions (amount of water converted/total amount of injected water) at 800°C – 57% and 81% respectively. Over-all the ASP materials exhibited both the highest water conversion and hydrogen yield. XRD spectra of SHS and ASP materials after water-splitting at 800 °C, are shown in Fig. 3. It can be seen that under these conditions samples from both routes are oxidized to the spinel phase and not to the tri-valent iron oxide Fe\(_3\)O\(_4\).

Because of the high activities of the SHS and ASP materials, similar reaction schemes were employed for the synthesis of other materials related to solar chemistry applications. A particular example is the synthesis of Ni-based catalysts for the solar-aided steam-reforming of natural gas. Current catalysts for these reactions consist of Ni metal supported on high-temperature-resistant mixed oxides of aluminum like MgAl\(_2\)O\(_4\), CaAl\(_2\)O\(_4\), or Ca\(_2\)Al\(_4\)O\(_7\) and are currently produced either via solid-state sintering of the respective oxides at elevated temperatures (>1500°C) or from wet chemistry routes that also involve sintering of precipitated powders (even though at lower temperatures). Both self-propagating and aerosol reaction schemes can be exploited for simultaneous in-situ synthesis of the mixed oxide support and reduction of Nickel oxide or Nickel nitrate respectively to Ni-metal, e.g. like the following:

\[
\text{SHS: } \ x\ NiO + 2k\ Al + (1-k)\ Al_2O_3 + y\ MgO + O_2 \rightarrow x\ Ni^+\ MgAl_2O_4 \quad \text{ ...(5)}
\]
SHS: \[ x \text{NiO} + k \text{Mg} + (1-k) \text{MgO} + \text{Al}_2\text{O}_3 + \text{O}_2 \rightarrow x \text{Ni}^{*}\text{MgAl}_2\text{O}_4 \] \[(6)\]  
SHS: \[ x \text{NiO} + 4k \text{Al} + 2(1-k)\text{Al}_2\text{O}_3 + \text{CaO} + \text{O}_2 \rightarrow x \text{Ni}^{*}\text{CaAl}_2\text{O}_7 \] \[(7)\]  
ASP: \[ x (\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}) + 2 \text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O} + \text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O} \rightarrow x \text{Ni}^{*}\text{CaAl}_2\text{O}_7 \] \[(8)\]

Figure 2: Comparison of “best” redox powders from each synthesis route with respect to: (a) water conversion and (b) total Hydrogen yield.

Figure 3: Phase composition comparison of redox powders before and after water-splitting at 800 °C: (a) SHS, (b) ASP materials.

XRD spectra of products of reactions (6-8) are compared in Fig. 4. Under appropriate reactants stoichiometry (by adjusting the Al/Al\(_2\)O\(_3\) or Mg/MgO ratio) several reaction schemes can be not only self-propagating but able to synthesize directly metal Ni supported on mixed oxides even though in some cases, quantities of reactants like MgO or Al\(_2\)O\(_3\) still remain in the products’ phase. Currently, such powders are under steam-reforming catalytic evaluation.

Figure 4: Phase composition comparison of mixed-oxide-supported Ni catalysts synthesized from various SHS reaction schemes.
Coating of porous supports

For the water-splitting case, extruded multichannel honeycombs with cell density of 90 channels per square inch (cpsl) from recrystallized and Silicon-metal-infiltrated (siliconized) Silicon Carbide (abbreviations reSiC and SiC respectively), manufactured by Stobbe Tech Ceramics, Denmark, were evaluated with respect to pore structure and thermomechanical properties both in the “as-manufactured” state as well as after prolonged operation as solar thermal collectors under solar irradiation in order to understand the phenomena that take place under exposure to solar irradiation, increase the lifetime of exposed receiver elements, and tailor their properties to those of the active coating materials. The detailed comparison results are the subject of another future publication; here only results relevant to porous structure in the “as-manufactured” state that are relevant to the coating process are reported.

The morphologies of two representative “as-manufactured” reSiC and siSiC samples are compared in Figs. 5a,5b. In the case of reSiC a binding phase is employed to “hold” the SiC grains together occupying some of the void space between them, however a residual porosity still exists, not only between the grains but also within the binding phase itself. The microstructure of siSiC is entirely different: elongated Silicon grains can be observed occupying most of the void space between the SiC grains and reducing significantly the inter-granular porosity. This difference can be clearly seen on the mercury porosimetry curves of the two materials (cumulative and differential) compared in Fig.1c. It can be seen that siSiC honeycombs are much denser than reSiC ones: their porosity is almost an order of magnitude lower - 3.8 % vs 36 %. Their mean pore size is higher though (35 μm vs. 6 μm), a fact indicating that some inter-granular space has not been infiltrated with Si. These two materials not only have different porosities but different thermal conductivities as well; therefore the support material can affect both the redox material loading achieved per impregnation, as well as the thermal behaviour of the reactor.

![Figure 5](image-url) (a) SEM photograph of reSiC honeycomb, (b) SEM photograph of siSiC honeycomb, (c) comparison of pore structure characteristics of the two supports.

The next step involved coating of SiC honeycombs with the synthesized materials via the “washcoating” technique employed for the coating of automotive catalysts, in which the porous supports are impregnated in a slurry of the coating powder [16]. Slurries of the SHS-synthesized powders were prepared with solids content varying between 50-80 wt% and stabilized with the aid of suitable dispersants. Small test-size siSiC and reSiC honeycomb pieces (Ø 25mm, 90 cpsl, length 15-50 mm) were impregnated in the powder slurries, dried and fired at 800 °C under nitrogen atmosphere to ensure efficient adhesion of the redox powder upon the substrate while retaining its oxygen-deficient structure. The effect of slurry solids content on the loading of the support with the redox material and on the homogeneity and reproducibility of the coatings was studied. The average values of loading efficiency (wt % of coating material with respect to the weight of the dry monoliths) for three coated samples for each case, are shown in Fig. 6a as a function of slurry solids content and support porosity. For the same slurry solids content, higher loadings are achieved on the material with higher porosity. Slurries with 80 wt% solids content were highly viscous, coatings were non-homogeneous and not reproducible; however with slurries of 70 wt% solids, reproducible and adequate loadings (about 13 wt% for siSiC and 25 wt% for reSiC samples) with a single impregnation were obtained. The thickness of the coating layer for the latter case was of the order of 200 μm. From the XRD spectra of a ZnFe₂O₄ coating powder before and after firing under inert atmosphere at 800 °C, shown in Fig. 6b, it can be clearly seen that such firing maintains the active state of the redox material and prevents the conversion of bi-valent iron to trivalent.

These coated honeycombs were employed for the first experimental campaign in the solar furnace to demonstrate the “proof-of-concept” of the proposed approach and to “screen” redox material formulations. Different “families” and “generations” of redox pair materials coated on such small-scale honeycombs were
evaluated in a solar test reactor that was designed and built at the German Aerospace Center DLR, Cologne, Germany. Two solar campaigns have proved beyond any doubt the proposed concept: not only the reactor was capable for producing hydrogen from steam at the expense of solar energy alone, but multi-cyclic operation (water splitting and redox material regeneration) at the temperature range 800-1200 °C was successfully demonstrated several times and for several of the redox materials synthesized [26].

Figure 6: (a) Coating loading (wt %) per impregnation as a function of slurry solids content and support porosity, (b) XRD of mixed iron oxide before and after adhesion firing.

To improve on long-term stability of the coating/support assembly and to prevent any reactions between the redox powder and the support material, a «next generation» of coated honeycombs was prepared by applying an intermediate coating layer on the monolith before that of the redox material, to offer structural and chemical stabilisation. Fully Yttria Stabilized Zirconia (YSZ, ZrO$_2$ containing 8 mol% / 13.27 wt% of Y$_2$O$_3$) was used for that intermediate layer. Pure zirconia has a high melting point (2,700°C) but a low thermal conductivity. The existence of yttria in its structure results in a solid solution of cubic lattice that does not exhibit any phase transformation during heating and cooling. It has been reported that addition of zirconia to a ferrite redox powder has helped in suppressing sintering of the ferrite and enhanced its reactivity. [27] The procedure used for the coating of that prime layer on the monoliths was the same as the one used for the redox powder coating: impregnation of the supports in ZrO$_2$ slurries (washcoating), drying of the coated support and finally firing at 700°C for 4 hours. ReSiC monoliths were first impregnated in ZrO$_2$ slurries, dried, fired, and subsequently impregnated in Zn$_x$Fe$_{1-x}$O slurries, some of them more than once in order to obtain honeycombs with different redox material loadings (Fig. 7). After each loading step with the redox material, the coated monoliths were fired under inert atmosphere at 800 °C for 2 hours. Characteristic SEM photographs of such a monolith are shown in Figs. 8a-8c, from where it can be clearly seen that the ZrO$_2$ layer interpolates between the monolith and the redox material and isolates them. Three small samples - using an intermediate layer of ZrO$_2$ for stabilisation and coated with Zn$_y$Fe$_{1-y}$O - were irradiated in the reactor to evaluate the performance of this third generation of coated monoliths. The detailed results are reported elsewhere [28], however it can be briefly stated here that these “next generation” coated honeycombs have demonstrated cyclic water-splitting/regeneration operation for 40 cycles, providing an almost constant amount of hydrogen and showing only minor evidence of coating quality deterioration. Current efforts are targeted in optimizing the oxide coating loading and determining the kinetics of the water-splitting and regeneration reactions.

Figure 7: (a) Coating loading (wt %) of six monoliths impregnated first in YSZ and then in Zn$_y$Fe$_{1-y}$O slurry.
For the steam reforming case, SiC foam supports were coated with MgAl$_2$O$_4$-supported Ni catalytic materials with a similar procedure (washcoating, adhesion firing). Typical photographs of the "first generation" of such coated foams (without having optimized the coating process) before and after aging (reduced in 5% H$_2$/N$_2$ at 1000°C for 10 hours) are shown in Fig. 9. The SEM picture in Fig. 9a indicates a rather poor quality coating, however since the encouraging fact is that the coated foams exhibit high absorbitivity (due to the black colour of the Ni metal after reduction), currently optimization of the coating process is in progress to provide uniform and adherent catalytic and absorbing coatings.

Figure 8: SEM photographs of a monolith that was impregnated once in a zirconia slurry and twice in a Zn$_x$Fe$_{1-x}$O slurry: (a) "top" view of coated channels, (b), (c) "top" and "front" view magnifications of the support/coating interphase.

Figure 9: Foams coated with MgAl$_2$O$_4$-supported Ni catalytic materials: (a) SEM photograph, (b) foam after loading, (c) same foam after aging.

Modelling and simulation

Even though the experimental results are encouraging, in order to scale-up the whole process, parameters such as the reactor volume, the loading with the oxide coating required and the cycle length have to be optimized, taking into account the solar flux and the resulting temperature distribution, the heat transfer characteristics, the reaction rates and transient phenomena due to reactor operation at alternating solar flux conditions. An important point that has to be quantified is the influence of reaction enthalpies on the operational behaviour. For instance, during the exothermic water splitting process, due to inadequate heat dissipation, hot spots might arise within the reactor, that can cause reaction (2) above to take place simultaneously with reaction (1) and introduce undesirable oxygen in the product stream. Therefore, in parallel to the experimental work, a mathematical model for the description of the cyclic water-splitting/regeneration process was formulated to describe the water-splitting process towards the production of hydrogen, inside a honeycomb monolithic reactor under the influx of solar radiation on its front face. The model includes the basic mass, momentum and energy transport processes as well as the heterogeneous surface reactions of water vapour with the redox coating on the channels of the reactor. Emphasis is placed on identifying the design factors of the monolithic reactor affecting its thermal response during its cyclic operation between water-splitting and coating regeneration cycles. Reactor operation simulations have demonstrated the important role of the thermal conductivity of the reactor material in distributing not only the incoming solar energy but also the heat of the water-splitting reaction along its length \[29\]. These factors have to be taken into account to prevent the regeneration reaction to take place simultaneously with the water-splitting one and to over-all optimize the reactor design and the operational cycle.
Conclusions

Material synthesis routes and chemical reactor concepts and technologies having already demonstrated their success and established in other areas, can be «transferred» to solar chemistry applications for the realization of solar hydrogen production, taking of course into account the peculiarities of high-temperature cyclic operation of solar reactors. A successful example is the development of a honeycomb solar reactor for the production of solar hydrogen via water-splitting that resembles the well-known automobile catalytic converters for the treatment of pollutant gases. Such a realization is based on the combination of two novel concepts: materials with very high water-splitting activity and regenerability (synthesised by novel short-time aerosol processes and combustion techniques) and their incorporation as coatings into special refractory ceramic monolithic reactors with high capacity for absorption of solar heat.

A wide variety of iron-oxide-based redox pair systems was synthesized via aerosol and combustion technologies, characterized and comparatively evaluated with respect to water splitting and regeneration capability. The synthesized systems were able to split water and generate Hydrogen as the only product, at temperatures as low as 800 °C with conversions reaching 80 % in terms of water (amount of water converted/total amount of water) and could be repeatedly regenerated under inert atmospheres at temperatures below 1200°C. Coating techniques were successfully employed for the preparation of multi-layer, multi-functional coatings on porous ceramic supports, meeting the thermomechanical operation demands of solar reactors. Similar synthesis routes have been explored and are currently optimized for the synthesis of other solar-chemistry related catalyst formulations such as Ni supported on MgAl2O4 for natural gas solar-aided steam reforming.

This approach resulted in an integrated solar reactor concept for the exploitation of solar heat via solar chemistry, which has never before been proposed or realized. The developed solar reactor not only produces hydrogen but also employs the use of renewable solar energy without any CO_2 emissions, in an entirely “clean”, natural and environmentally friendly way. In fact the current technology is a demonstration of solar chemistry-based hydrogen production from water, with a future potential - especially when employed in combination with other solar thermal applications (in particular power plants) - to achieve a hydrogen cost below 0.10 Euros/kWh (in the long-term). The technology of catalytic solar reactors proposed can be advantageously integrated in such plants, offering the potential of solar energy storage and transport of the generated hydrogen to consuming sites.

However, even though the “proof-of-concept” has been demonstrated, further fine-tuning and optimization of the process parameters via parallel experimental and modelling work is needed for an efficient process scale-up. A mathematical model formulated to describe the water-splitting process inside such a reactor under the influx of solar radiation on its front face, has demonstrated the important role of the thermal conductivity of the reactor material in distributing not only the incoming solar energy but also the heat of the water-splitting reaction along its length. These factors have to be taken into account to prevent the regeneration reaction to take place simultaneously with the water-splitting one and to over-all optimize the reactor design and the operational cycle.

Acknowledgements


References:


[21] Steinfeld, A., Sanders, S., Palumbo, R.,...